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## VAPOR PHASE HYDROLYSIS OF PENTABORANE-9

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WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Contract Monitors: A. A. Thomas and K. C. Back  
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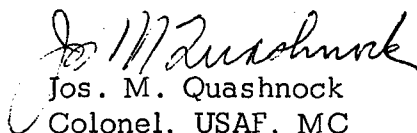
This study was initiated by Project TORES (Toxicology Research) under the sponsorship of the Advanced Research Projects Agency, DOD, and procured by the U. S. Army Chemical Center, Maryland. Upon termination of Project TORES, procurement and administrative functions were transferred to the Aerospace Medical Division, AFSC, Brooks AFB, Texas. Technical monitoring was delegated to the Toxic Hazards Branch, 6570th Aerospace Medical Research Laboratories, Wright-Patterson AFB, Ohio. The research was performed in support of Project 6302, "Toxic Hazards of Propellants and Materials," Task 630202, "Pharmacology and Biochemistry," from 1 June 1962 to 31 May 1963. Dr. C. H. Wang was the principal investigator for Oregon State University and Drs. A. A. Thomas and K. C. Back were contract monitors for the 6570th AMRL.

## ABSTRACT

The hydrolysis of pentaborane-9 in the vapor phase was carried out at 85° C and 150° C. The reactions carried out at 150° C were at initial pentaborane concentrations in a ratio of 10 to 1 with a constant water concentration. Since these reaction conditions gave initial rate constants in a ratio of 10 to 1, it was concluded that the vapor phase hydrolysis of pentaborane was initially first order in respect to pentaborane concentration. A proposed mechanism for the reaction suggests an initial hydrolysis of the terminal hydrogen atoms of pentaborane at a decreasing rate followed by the rupture of the pyramidal boron framework and/or hydrolysis of the bridge hydrogen atoms at an accelerated rate.

## PUBLICATION REVIEW

This technical documentary report is approved.

  
Jos. M. Quashnock  
Colonel, USAF, MC  
Chief, Biomedical Laboratory

# VAPOR PHASE HYDROLYSIS OF PENTABORANE-9

## I. INTRODUCTION

Pentaborane is a stable boron hydride having the molecular formula  $B_5H_9$ . A pyramidal structure (ref. 2 & 10) for pentaborane has been established by x-ray diffraction methods (ref. 3), by electron diffraction methods (ref. 5), and by microwave spectroscopy studies with the gas (ref. 6). Four hydrogen atoms form single hydrogen-bridge bonds between the four boron atoms at the base of the pyramid and each of these boron atoms are linked to a single hydrogen atom by a normal boron-hydrogen bond. Thus, there are two different types of bonds to hydrogen in pentaborane; four basal bridge bonds and five terminal boron-hydrogen bonds. Of the terminal boron-hydrogen bonds, the one at the apex of the pyramidal structure has been shown to be most reactive (ref. 8, 9, & 11). The structure is represented by figure 1, below.

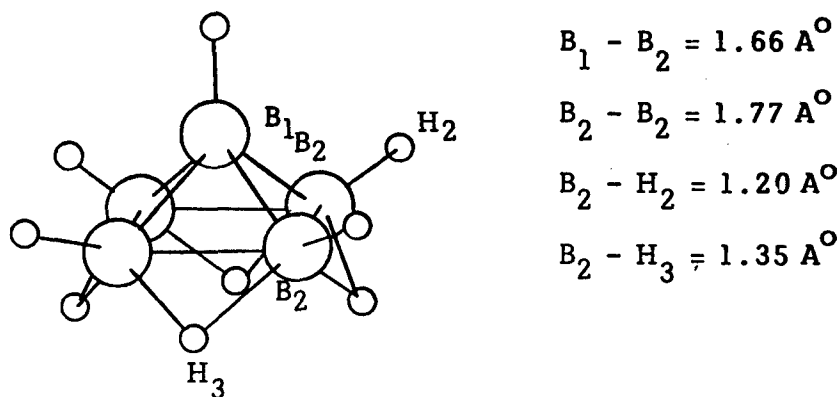
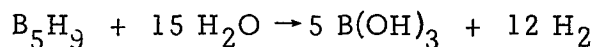


Figure 1. Pyramidal Pentaborane Structure

Kinetic studies of the reaction of pentaborane are very incomplete due in part to the pyrophoric and toxic properties of pentaborane. Shapiro and Weiss (ref. 14) reported that pentaborane hydrolysis by water was very slow at room temperature and required several hours contact with water at  $90^\circ \text{C}$  for complete hydrolysis. Since the slow hydrolysis rate was due to the immiscibility of pentaborane with water, dioxane was used as a mutual solvent. Hydrolysis reactions in an 80 percent dioxane-water mixture were complete in minutes and were too rapid for accurate kinetic determinations, but did suffice to establish the stoichiometry of the reaction. According to hydrogen production measurements, the hydrolysis reaction is represented as:



Shapiro and Weiss (ref. 13) later proposed that the first step in the hydrolysis of pentaborane was the removal of a borine group ( $\text{BH}_3$ ) by water with the subsequent reaction of the borine group with water to produce hydrogen. The proposed mechanism suggested the removal of a basal boron atom from the pyramidal pentaborane structure, which left the molecular skeleton of a tetraborane ( $\text{B}_4\text{H}_{10}$ ) molecule.

More recent reports (ref. 8 & 11) have shown that hydrogen-deuterium exchange reactions of pentaborane proceed preferentially in the terminal hydrogen positions with the apex terminal hydrogen atom being the most reactive, and that the bridge hydrogen atoms do not participate in the exchange at all. Another worker (ref. 9) states that halogen substitution takes place preferentially at the apex boron atom of pentaborane. From this evidence, it would appear likely that the hydrolysis of pentaborane initially proceeds by the hydrolysis of the terminal hydrogen atoms rather than by the rupture of the pentaborane skeleton as proposed by Shapiro (ref. 13). Shapiro (ref. 1) studied the oxidation of pentaborane and was able to isolate and identify an intermediate product with the formula  $\text{H}_2\text{B}_2\text{O}_3$ . From this it was concluded the oxidation reaction mechanism was very similar to the mechanism for pentaborane hydrolysis.

The present work was designed to study the kinetics of the hydrolysis of pentaborane. Initially, however, a method was devised whereby the hydrolysis reaction would proceed at a readily measurable rate in the vapor phase to maintain a homogeneous system and thus simplify the reaction system with respect to reaction kinetics. These conditions avoided such complications as the immiscibility of pentaborane with water, the introduction of a mutual solvent, and the possibility of an interface surface reaction in the liquid phase hydrolysis.

The work presented is an initial phase of a research program on the toxicity of pentaborane to mammals. The kinetics and mechanism of pentaborane hydrolysis are being utilized in determining the fate of pentaborane in biological systems.

## II. MATERIALS AND METHODS

Pentaborane used in these experiments was obtained from the Callery Chemical Company, Callery, Pennsylvania.

A high vacuum manifold system was used for the handling of pentaborane according to the procedures described by Sanderson (ref. 12). The system was manufactured by the Delmar Company, Maywood, Illinois. The quantity of pentaborane for each experiment was accurately determined by measuring the pressure of gaseous pentaborane in calibrated volumes of the high vacuum system at room temperature.

The reactions were carried out either in an excess of water or with stoichiometric quantities of both reactants according to the reaction for complete hydrolysis. Distilled water was used for all the reactions. The water was accurately weighed in a small evacuated weighing bulb for the reactions

of the stoichiometric quantities of the reactants. For the reactions in an excess amount of water, the water was measured by pipette and then transferred to the reaction flask under a high vacuum. The reaction rate was conveniently followed by measuring the production of hydrogen gas at the end of a predetermined reaction interval. Pentaborane has been reported to be stable up to  $180^{\circ}\text{C}$  (ref. 4) so the hydrolysis reactions were performed at somewhat elevated temperatures. Several hydrolysis reactions were carried out at  $25^{\circ}$ ,  $70^{\circ}$ ,  $85^{\circ}$ , and  $150^{\circ}\text{C}$ , respectively. The hydrolysis rate was not appreciable below  $150^{\circ}\text{C}$  so the majority of the reactions were carried out at this temperature.

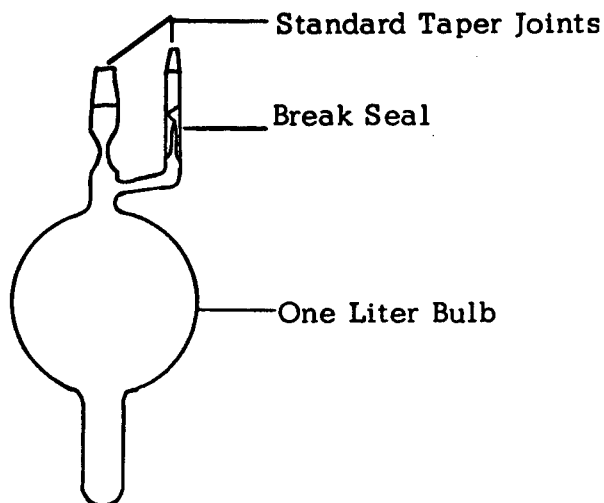


Figure 2. Hydrolysis Flask

A one-liter hydrolysis flask, shown in figure 2, was evacuated and the measured quantities of pentaborane and water were condensed into the flask by the use of liquid nitrogen. The flask was sealed, warmed to room temperature, and then placed in an oven preheated to  $190^{\circ}\text{C}$ . Four to five minutes were required for the flask to reach an equilibrium temperature of  $150^{\circ}\text{C}$ , at which time the initiation of the reaction was recorded. The reaction was terminated by cooling the hydrolysis flask with tap water and then placing the flask in a Dewar flask containing liquid nitrogen. The process for the termination of the hydrolysis reaction required a maximum of two minutes. The flask was then attached to the high vacuum system, using the side arm standard taper joint, the break seal broken, and the hydrogen transferred out and measured by manometric techniques. A liquid nitrogen trap was placed between the Toepler pump and the flask in order to trap any condensable material that did not remain in the flask.

### III. RESULTS

Figures 3 and 4 show graphically the data given in table I in which pentaborane hydrolysis was examined at  $85^{\circ}\text{C}$ . It can be seen that the

reaction under these conditions is first order in respect to pentaborane concentration.

TABLE I

PENTABORANE HYDROLYSIS IN AN EXCESS AMOUNT  
OF WATER AT  $85^{\circ} \pm 2.0^{\circ} \text{C}$

Time (hours)	Initial mM $\text{H}_2\text{O}$	Initial mM $\text{B}_5\text{H}_9$	mM $\text{H}_2$	Remaining* mM $\text{B}_5\text{H}_9$	Percent Completion
2.3	16.65	0.199	0.049	0.196	2.0
3.4	16.65	0.198	0.058	0.194	2.4
7.2	16.65	0.197	0.097	0.189	4.1

\* Calculated from the amount of hydrogen gas produced.

From the slope of the graph of figure 4 an initial rate constant of  $-0.0143 \text{ mM B}_5\text{H}_9/\text{hour}$  was obtained.

Figures 5 and 7 are graphs of the data given in table II. In these experiments, the hydrolysis reaction was carried out with excess water at  $150^{\circ} \text{C}$ . The initial rate constant calculated from the data in figure 7 is  $-0.064 \text{ mM B}_5\text{H}_9/\text{hour}$ . Again the reaction is initially first order in respect to pentaborane concentration.

Figures 6 and 8 are graphs of the data given in table III. In these experiments the hydrolysis reaction was carried out with a stoichiometric concentration of water at  $150^{\circ} \text{C}$ . The initial rate was determined by the slope of the graph of figure 8 and is  $-0.650 \text{ mM B}_5\text{H}_9/\text{hour}$ .

The vapor pressure of pentaborane was determined at  $0^{\circ} \text{C}$  to ascertain its purity and was found to be 65.5 mm Hg. The published value (ref. 4) is 65 mm Hg. A control experiment in which 0.5 mM  $\text{B}_5\text{H}_9$  was heated at  $150^{\circ} \text{C}$  for seven hours produced only 0.25 percent of the theoretical total amount of hydrogen according to the complete decomposition reaction of pentaborane (ref. 7). Since this hydrogen production was small in comparison to the total hydrogen produced in the experiments, its effect was considered negligible.



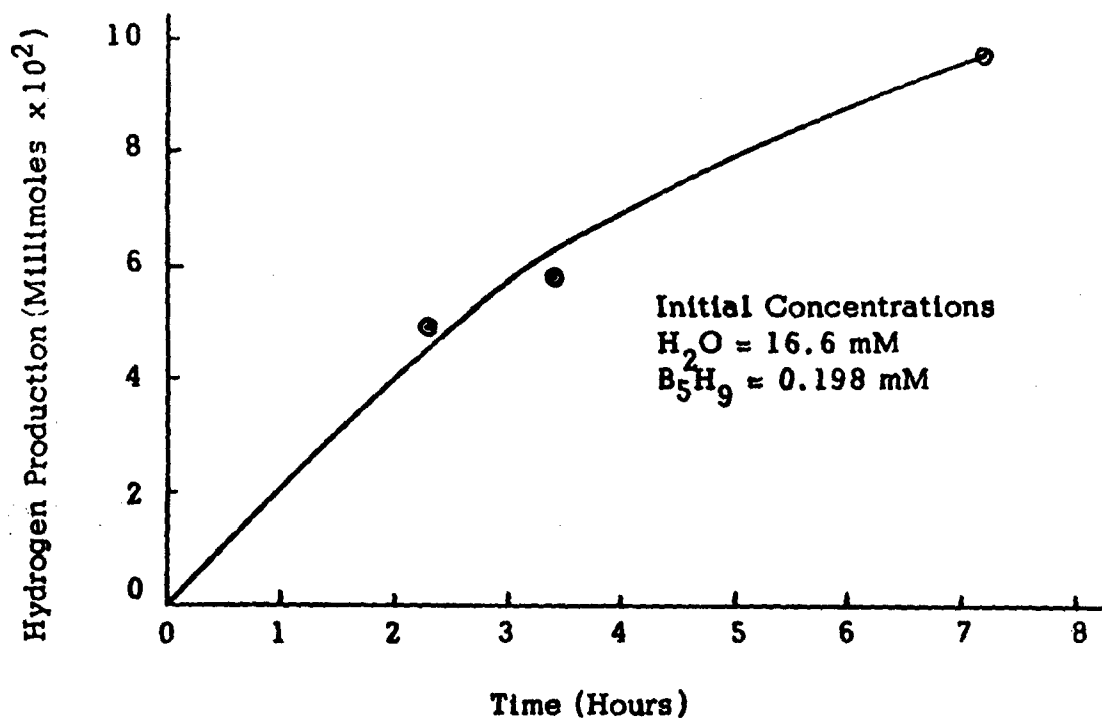


Figure 3. Plot of Hydrogen Production of Pentaborane Hydrolysis Reaction in Excess Water at  $85^\circ\text{C}$ .

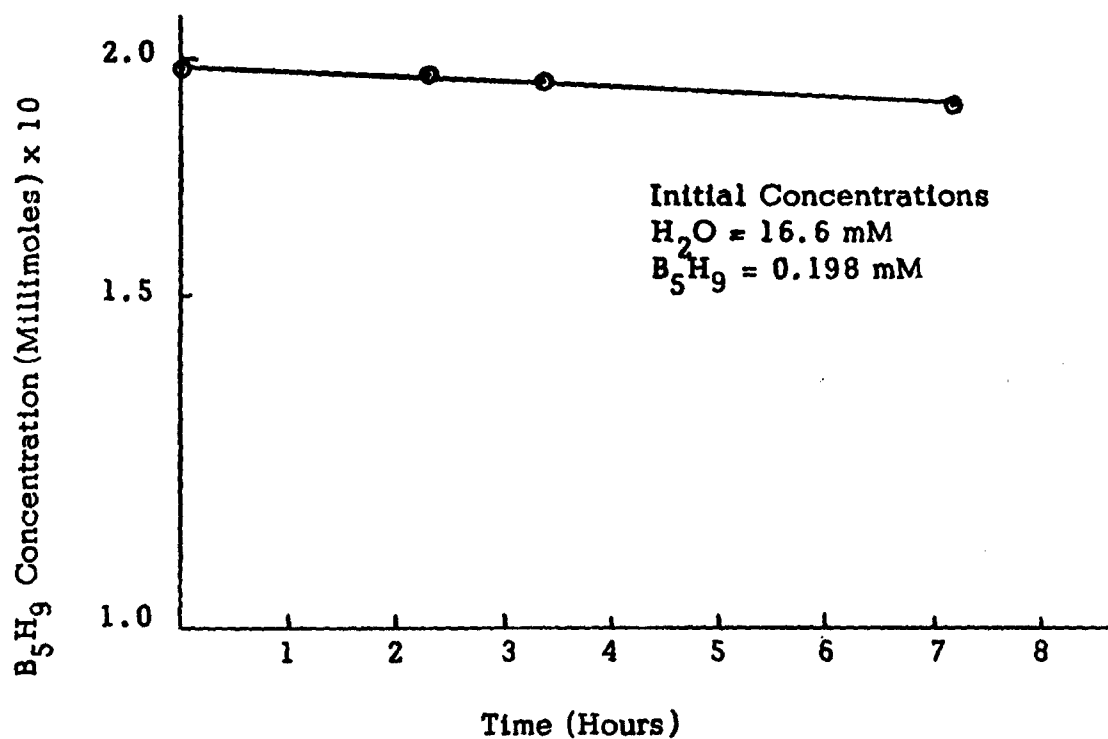


Figure 4. Semilogarithmic Plot of Pentaborane Hydrolysis Reaction in Excess Water at  $85^\circ\text{C}$ .

TABLE II

PENTABORANE HYDROLYSIS IN AN EXCESS AMOUNT OF WATER AT  $150^{\circ} \pm 2.0^{\circ} \text{C}$ 

Time (hours)	Initial $\text{mMB}_5\text{H}_9$	$\text{mMH}_2$ Formed	Remaining* $\text{mMB}_5\text{H}_9$	Initial $\text{mMH}_2$	Remaining* $\text{mMH}_2\text{O}$	Percent Completion
0.5	0.369	0.37	0.338	55.5	55.0	8.4
1.0	0.372	0.79	0.306	55.5	54.5	17.7
2.0	0.370	1.32	0.261	55.5	53.9	29.6
3.0	0.368	1.41	0.250	55.5	53.7	32.0
4.0A	0.370	1.72	0.226	55.5	53.4	38.7
4.0B	0.371	1.65	0.234	55.5	53.4	37.0
4.5	0.370	2.26	0.182	55.5	52.7	50.9
5.0	0.370	2.44	0.166	55.5	52.4	55.0
6.0	0.370	2.70	0.145	55.5	52.1	60.8
7.0	0.370	2.85	0.132	55.5	51.9	64.3
8.0	0.370	3.11	0.111	55.5	51.6	70.2

\* Calculated from the amount of hydrogen gas produced.

TABLE III

STOICHIOMETRIC HYDROLYSIS OF PENTABORANE AT  $150^{\circ} \pm 2.0^{\circ} \text{C}$ 

Time (hours)	Initial $\text{mMB}_5\text{H}_9$	$\text{mMH}_2$	Remaining* $\text{mMB}_5\text{H}_9$	Initial $\text{mMH}_2\text{O}$	Remaining* $\text{mMH}_2\text{O}$	Percent Completion
0.5	3.74	3.04	3.48	55.87	52.07	6.8
1.0	3.76	6.30	3.24	55.73	47.85	14.1
2.0	3.75	8.70	3.03	56.10	45.27	19.4
3.0A	3.73	9.83	2.91	56.12	43.82	22.0
3.0B	3.75	10.30	2.89	56.27	43.41	22.9
4.0A	3.76	12.11	2.75	55.99	40.84	27.0
4.0B	3.76	12.45	2.72	55.88	40.28	27.8
5.0	3.76	14.58	2.55	55.92	37.77	32.6
6.0	3.76	15.86	2.44	56.06	36.30	35.4
7.0	3.74	19.03	2.15	56.17	32.32	42.4
8.0	3.77	20.12	2.09	56.01	30.81	44.9

\* Calculated from the amount of hydrogen gas produced.

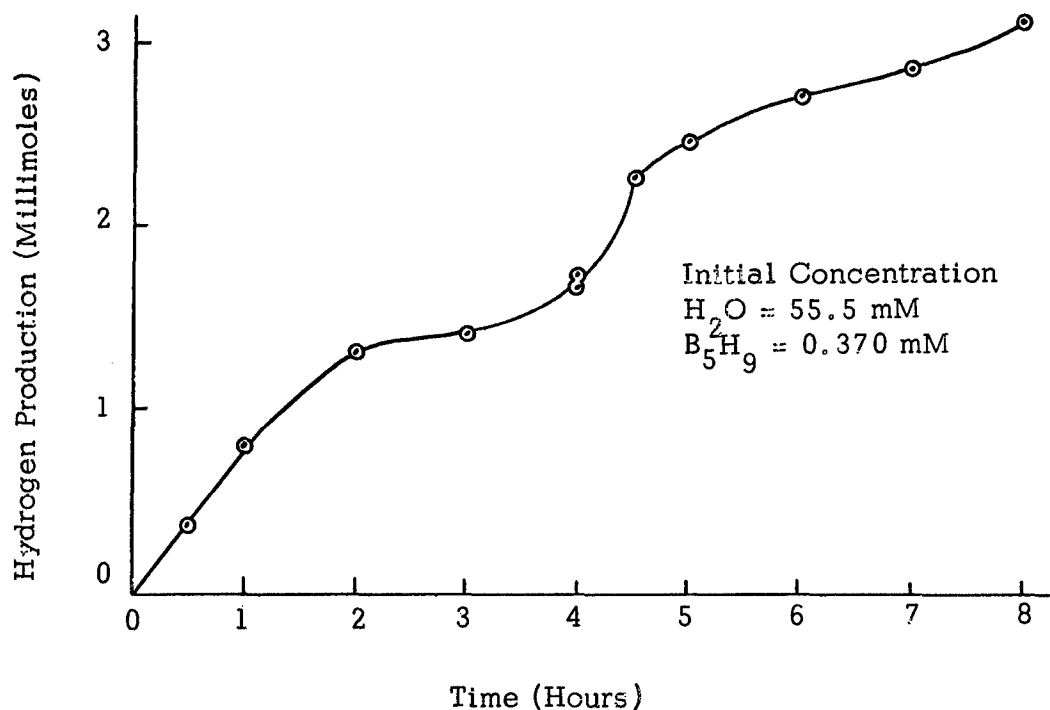


Figure 5. Plot of Hydrogen Production of Pentaborane Hydrolysis Reaction in Excess Water at  $150^\circ\text{C}$ .

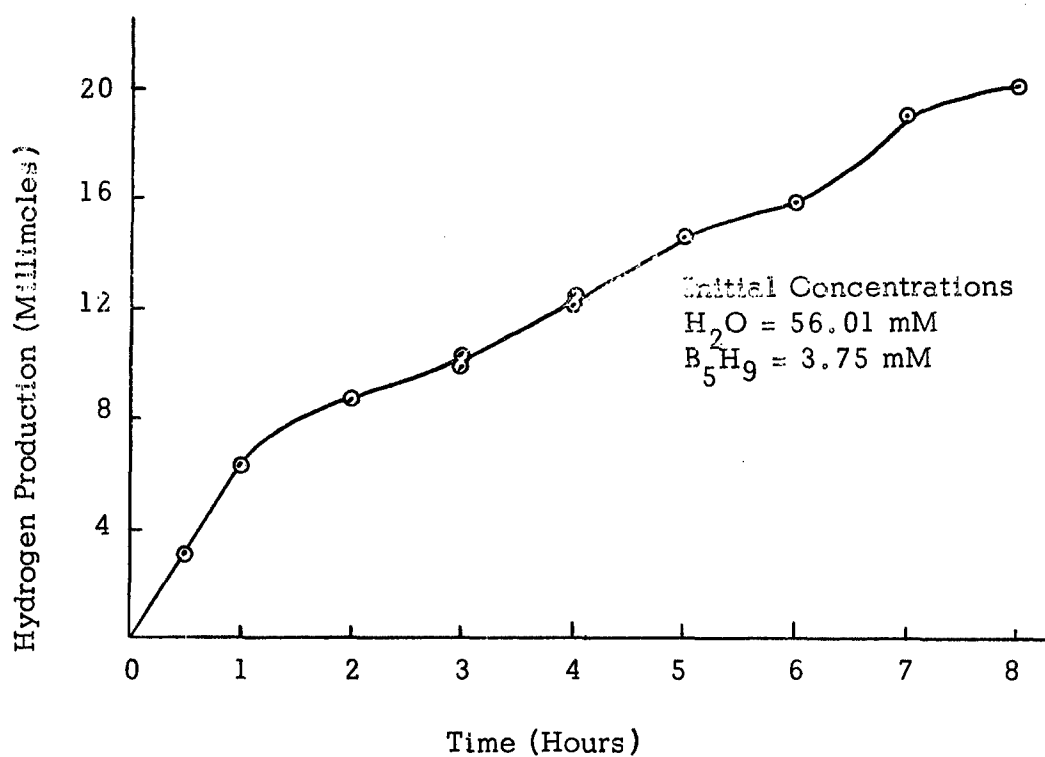


Figure 6. Plot of Hydrogen Production of Stoichiometric Pentaborane Hydrolysis Reaction at  $150^\circ\text{C}$ .

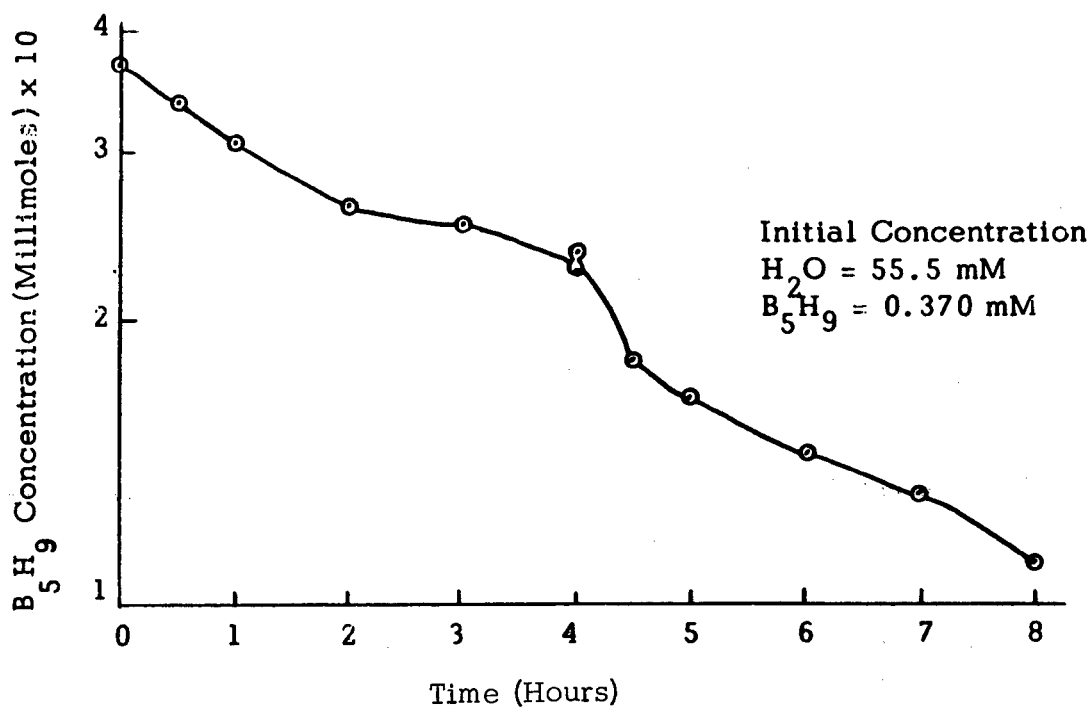


Figure 7. Semilogarithmic Plot of Pentaborane Hydrolysis Reaction in Excess Water at  $150^\circ\text{C}$ .

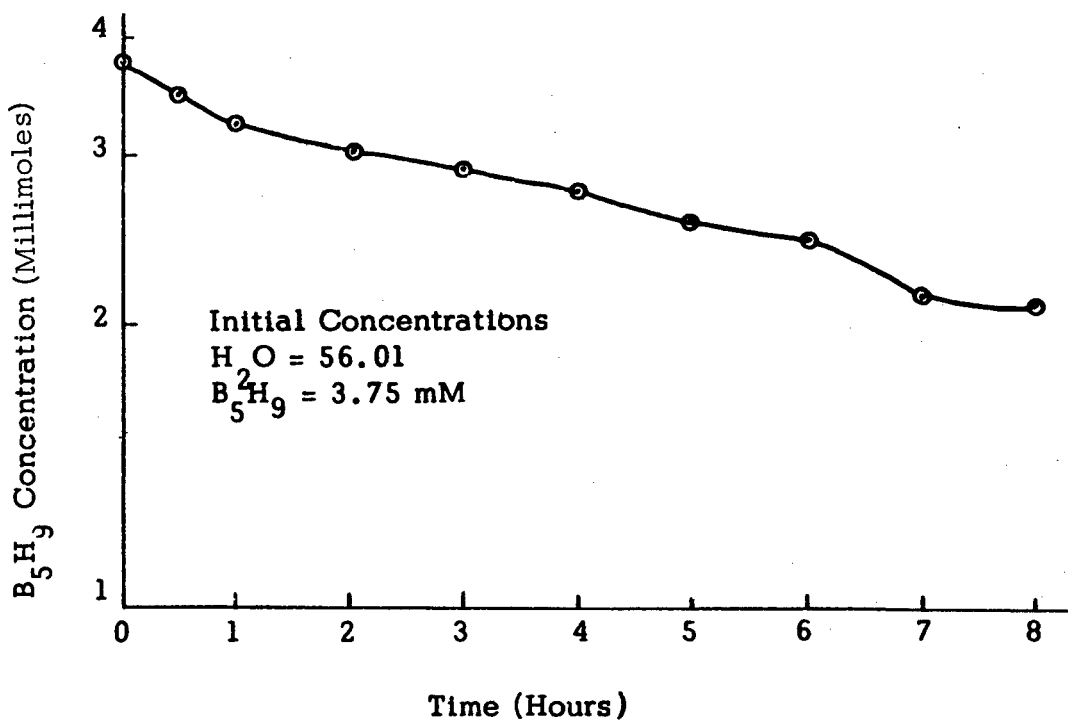


Figure 8. Semilogarithmic Plot of Stoichiometric Pentaborane Hydrolysis Reaction at  $150^\circ\text{C}$ .

#### IV. DISCUSSION

In the two experiments performed at 150° C, with respective initial concentrations of pentaborane in a ratio of 10 to 1 and with a constant concentration of water, the results gave respective initial rate constants also in a ratio of 10 to 1. It was thus concluded that the vapor phase hydrolysis of pentaborane was initially first order with respect to pentaborane concentration.

It is quite significant that an acceleration in the reaction rate occurs in both cases at 150° C (figures 6 & 7) at nearly the same stage--a point corresponding to about 41 percent completion of the reaction. This percent corresponds to a ratio of 5 to 12. Pentaborane contains five terminal hydrogen atoms and the complete hydrolysis reaction produces twelve moles of hydrogen per mole of pentaborane. A possible reaction mechanism would be the initial hydrolysis of the terminal hydrogen atoms at a decreasing rate followed by the rupture of the boron framework and/or the hydrolysis of the bridge hydrogen atoms at an accelerated rate. The complete hydrolysis reaction would first give rise to five moles of hydrogen from the terminal hydrogen atoms, then four moles of hydrogen from the hydrolysis of the bridge hydrogen atoms, and finally three moles from the hydrolysis of the boron framework itself.

The pentaborane hydrolysis reaction could obviously proceed through several intermediate products. Therefore, it is imperative that these intermediate products be isolated and identified before the hydrolysis reaction mechanism can be accurately determined.

The extremely slow rate of pentaborane hydrolysis in the vapor state suggests that Shapiro and Weiss (ref. 14) were observing effects of dioxane which are in addition to its solvent properties. The electron deficiency of the pentaborane molecule may cause its interaction with dioxane prior to hydrolysis by water. Hydrolysis of pentaborane by biological systems could also be expected to be due to its initial interaction with cellular constituents other than water.

#### V. SUMMARY

A study was made of the hydrolysis of pentaborane-9 in the vapor phase. The reactions were carried out at 85° and 150° C, respectively. It was found that the reaction was initially first order with respect to pentaborane concentration.

A proposed mechanism of the reaction suggests an initial hydrolysis of the terminal hydrogen atoms of pentaborane at a decreasing rate followed by the rupture of the boron framework and/or the hydrolysis of the bridge hydrogen atoms at an accelerated rate. The intermediate products of the hydrolysis reaction must be isolated and identified to characterize further the mechanism of the reaction between pentaborane and water.

## REFERENCES

1. Ditter, J. F. and I. Shapiro, "Identification of an Intermediate Compound in the Partial Oxidation of Pentaborane-9," Journal of the American Chemical Society, Vol 81, pp 1022-1024 1959.
2. Duffy, G. H. "The Pyramidal  $B_5H_9$  Structure," Journal of Chemical Physics, Vol 20, p 194, 1952.
3. Dulmage, J. and W. N. Lipscomb, "The Molecular Structure of Stable Pentaborane," Journal of the American Chemical Society, Vol 73, p 3539, 1951.
4. Goshgarian, B. B. and A. V. Jensen, A Study of Pentaborane, AFFTC-TR-61-34, May 1961.
5. Hedberg, K., M. Jones and H. Schömaker, "On the Structure of Stable Pentaborane," Journal of the American Chemical Society, Vol 73, pp 3538-3539, 1951.
6. Hrostowski, J. H., R. J. Myers and G. C. Pimentel, "The Microwave Spectra and Dipole Moment of Stable Pentaborane," Journal of Chemical Physics, Vol 20, p 518, 1952.
7. Johnson, W. H., E. J. Prosen, and F. Y. Pergiel, "Heats of Formation of Diborane and Pentaborane," Journal of Research of the National Bureau of Standards, Vol 61, pp 247-249, 1958.
8. Kaufman, J. J., W. S. Koski and P. C. Lauterbur, "Nuclear Magnetic Resonance Study of the  $B_2D_6$  -  $B_5H_9$  Exchange Reaction," Journal of the American Chemical Society, Vol 79, pp 2382-2385, 1957.
9. Lipscomb, W. N. "Structures and Reactions of the Boron Hydrides," Journal of Inorganic and Nuclear Chemistry, Vol 11, pp 1-8, 1959.
10. Lipscomb, W. N., "Structures of the Boron Hydrides," Journal of Chemical Physics, Vol 22, pp 985-987, 1954.
11. Onak, T. P. and R. E. Williams, " $B_5H_9$  - DCl Exchange Catalyzed by  $AlCl_3$ ," Inorganic Chemistry, Vol 1, p 106, 1962.
12. Sanderson, R. T., High Vacuum Manipulation of Volatile Compounds, John Wiley & Sons, New York, New York, 1948.
13. Shapiro, I. and H. G. Weiss, "First Step in the Hydrolysis of Pentaborane," Journal of the American Chemical Society, Vol 76, p 1205, 1954.
14. Shapiro, I. and H. G. Weiss, "Hydrolysis of Pentaborane," Journal of the American Chemical Society, Vol 76, pp 6020-6021, 1954.